Bipolaron Formation in Organic Solar Cells Observed by Pulsed Electrically Detected Magnetic Resonance

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We report the observation of a spin-dependent dark transport current, exhibiting spin coherence at room temperature, in a π-conjugated polymer-fullerene blend using pulsed electrically detected magnetic resonance. The resonance at $g = 2.0028(3)$ is due to polarons in the polymer, and exhibits spin locking at high microwave fields. The presence of an excess of fullerene, and the operating voltage (1 V) used, suppresses negative polaron formation in the polymer. It is concluded that spin-dependent transport is due to the formation of positive bipolarons.

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Organic semiconductors provide a range of commercial optoelectronic display devices, and show great promise in the field of photovoltaics (PV) [1–4] if improved efficiency, combined with low cost and ease of production, can be achieved. In addition, the weak spin-orbit coupling of organic semiconductors is attractive for carrier spin transport and manipulation, and is driving efforts to develop spintronic devices [5]. All these applications depend upon detailed knowledge of the relevant transport processes, in particular, those influenced by spin selection rules. The observation of large magnetoresistance (MR) has, for example, attracted a range of explanations [6–9], but aspects of the proposed mechanisms remain controversial [10].

Conduction in disordered organic semiconductors is dominated by hopping of charge carriers between localized states. Because of strong electron-phonon coupling the carriers are polarons. Oppositely charged polarons can form excitons and eventually recombine; the process normally depends on the spin state of the coupled pair immediately prior to exciton formation. In addition, the strong coupling between carriers and the environment can markedly reduce the energy cost of doubly occupying states. Two like-charge polarons can form a bipolaron, the correlation energy between the pair and the lattice deformation lowering the formation energy [11]. However, the on-site exchange requires that the final state is a spin singlet, and bipolaron formation will be ''spin-blocked'' if two polarons have the same spin component along the common axis of quantization [8].

Organic PV devices have advanced dramatically with the development of bulk heterojunction materials [2–4], which comprise a π-conjugated polymer blended with an electron acceptor such as a fullerene derivative. The two phase-separated components give interpenetrating networks with vastly increased interfacial regions [3]. The PV effect is due to photoexcitation of the polymer, followed by highly efficient electron transfer to the fullerene phase. Positive polarons (P^+) are transported through the polymer matrix, negative polarons through the fullerene phase, efficiently suppressing carrier loss by P^+P^- recombination. However, unipolar transport to the electrodes may be influenced by bipolaron formation. Gaining insight into this process, which affects charge carrier collection efficiency in solar cells and which may be responsible for MR [8], cannot be achieved on the basis of the electrical properties alone.

Here we detect resonant changes in charge transport through organic heterojunction solar cells, which can be attributed to spin-dependent bipolaron formation during hopping transport through the polymer, using electrically detected magnetic resonance (EDMR). The probability for bipolaron formation depends on the spin symmetry of the weakly coupled precursor P^+P^+ pair. An increase in the singlet content of the pairs, caused by a spin-resonant excitation, leads to an enhanced bipolaron formation probability, and thus facilitates the hopping transition of one P^+ to the site of the other. This process enables the previously blocked transport path and, in consequence, provides a resonant change in the detected current (the EDMR signal). Room temperature measurements on poly (2-methoxy-5-(2'-ethyl)-hexyloxy-*p*-phenylene) vinylene (MEH-PPV) : [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) devices operated in forward bias exhibit a continuous wave (cw) EDMR spectrum that can be resolved into two components. The resonance position ($g = 2.0028$) is in agreement with that for positive polarons [12], and precludes any significant involvement of PCBM centers ($g = 1.9995$). Pulsed EDMR (pEDMR) measurements at high microwave (mw) field intensities exhibit spin locking and show that the resonant spin-dependent transport

process involves coupled $S = 1/2$ pairs. Spin-coherent Rabi oscillations are also detected and quantify spin locking, giving further insight into the mechanism of bipolaron formation.

The solar cells were fabricated on indium tin oxide (ITO) coated glass substrates. After cleaning and structuring the ITO electrodes, a single layer consisting of MEH-PPV and PCBM was spin-coated from a solution in chlorobenzene in the ratio of 1:4 (by weight). A 100 nm thick Al layer was then deposited giving an active device area of 5 mm^2. The electrodes extended along the length of the substrate to bring them out of the mw resonator. EDMR was performed using a Bruker E580 spectrometer at room temperature in the dark.

Figure 1(a) shows the cwEDMR spectrum of the bulk heterojunction solar cell obtained using a constant forward bias for charge carrier injection ($U = 1.0$ V, $I = 18.7$ μA). The spectrum is similar to cwEDMR spectra of MEH-PPV based diodes [13], except here we observe a relative increase in the current at resonance. Best fits [Fig. 1(a)] are obtained by assuming two resonances with $g = 2.0028(3)$, a narrow pseudo-Voigtian line shape (FWHM = 0.6(1) mT) and a wider Gaussian component (1.5(1) mT), with identical doubly integrated intensities [14]. The linewidths and g values agree with earlier EDMR and light-induced EPR measurements on polarons in PPV [12,15,16]. The g value excludes the possibility that

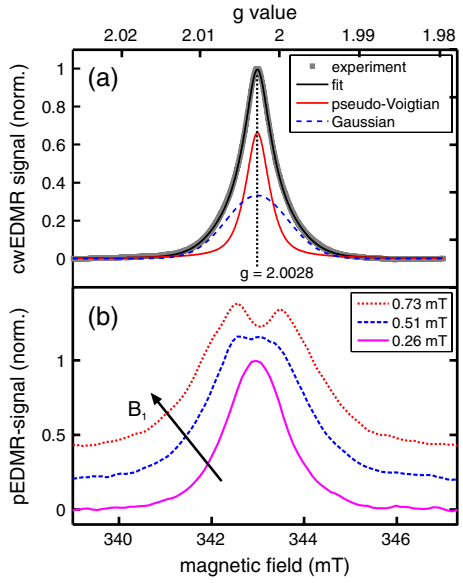

FIG. 1 (color online). (a) Integrated cwEDMR spectrum (gray squares) obtained at room temperature without illumination. The solid line represents a fit assuming two resonance lines with equal doubly integrated intensities and g values but different line shapes. The solid and dashed lines show the individual fit components. (b) B_1 dependence of the pEDMR spectrum (integrated current change following a 160 ns mw pulse, maximum relative current change: $\Delta I/I = 3 \times 10^{-5}$).

PCBM anions ($g = 1.9995$) are making a significant contribution to the spectrum [12].

The cwEDMR line shape shown in Fig. 1(a) may be explained by assuming two overlapping polaron populations, which differ in environment and/or mobility. Different environments lead to different g and hyperfine tensors. Immobile centers then give a Gaussian line, while polaron mobility may average the anisotropies leading to a pseudo-Voigtian line shape. The cwEDMR spectrum alone does not provide insight into the detailed microscopic mechanism. It could be due to bipolaron formation, but could also be consistent with recombination of triplet excitons at $S = 1/2$ trap centers. To provide further evidence on the spin-dependent transport mechanism, pEDMR was employed [17].

Figure 1(b) shows pEDMR spectra recorded for different amplitudes of the magnetic component of the mw field, B_1. For $B_1 < 0.26$ mT a single resonance line is observed. With increasing mw power this line broadens, and above 0.5 mT a "dip" emerges in the center of the resonance line. This is an indication of coupled spin pairs, where the resonance spectra of each member overlap. When B_1 is sufficiently high to simultaneously excite the EPR of both members of the pair, spin locking occurs [18]. The EDMR spectrum is often assumed to be due to the formation of $S = 1/2$ spin pairs as part of a transport process in which a rate constant is markedly higher for the singlet configuration, compared to the triplet states. The mw field then induces changes to the singlet and triplet populations away from equilibrium which manifest as a changing current [19]. In the case of spin locking the total spin of the pair of $S = 1/2$ centers is not altered by the mw field, there is a freezing of singlet (S) to triplet (T) conversion. The mw field simply shifts the population between the three triplet sublevels of the total spin $S = 1(T^+, T^0, T^-)$ [20,21]. The EDMR signal decreases since the S and T populations return to their steady-state values. This is observed as a dip in the center of the spectrum. While the observation of power-dependent line shape changes is persuasive, the spin-locking mechanism should also result in a characteristic behavior in the coherent precession about the B_1 field (Rabi oscillations).

Figure 2(a) shows pEDMR detected Rabi oscillations measured on resonance for different amplitudes of B_1. The oscillation amplitude is damped with a time constant $\sim$150 ns, which may be caused by spin relaxation of the individual spins, recombination or coherent dephasing due to B_1 inhomogeneities [19]. At low mw power ($B_1 = 0.26$ mT), the frequency of the oscillation ($\Omega/2\pi$) corresponds to the Rabi frequency, $\Omega = \gamma B_1$, where γ is the gyromagnetic ratio, which here is found to take the value due to a total spin 1/2, see Fig. 2(b). Rabi oscillations are detected because spin pairs initially in a triplet configuration ($|\uparrow\uparrow\rangle$ or $|\downarrow\downarrow\rangle$) in the steady state are increasingly driven into mixed states with application of the mw pulse with

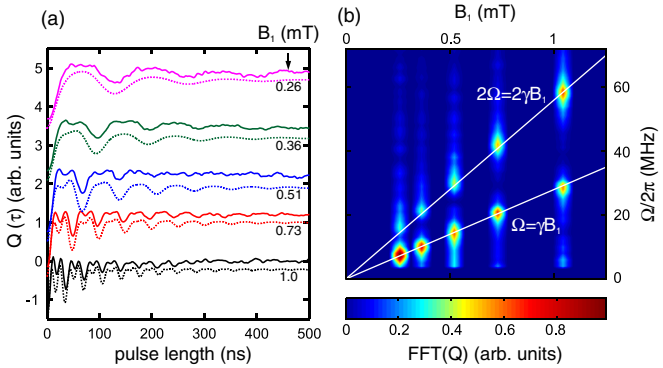

FIG. 2 (color online). Electrically detected spin-Rabi nutations obtained at room temperature. (a) Integrated charge Q as a function of the mw pulse length τ for several values of B_1 and simulation results for bipolaron formation (dotted curves, vertically offset downwards). (b) Fast Fourier Transform (FFT) of the data shown in (a). With increasing B_1 the intensity (represented by the color code) of the Ω component decreases whereas the intensity of the 2 Ω component increases.

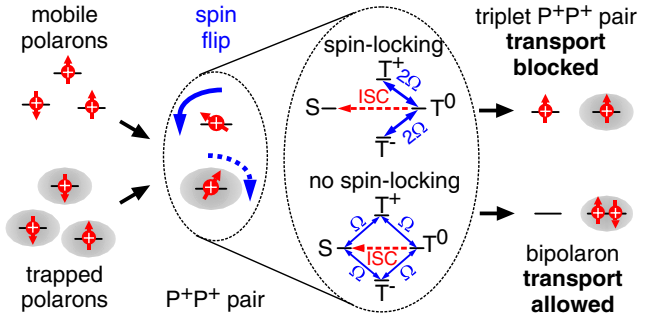

FIG. 3 (color online). Bipolaron formation under resonant microwave excitation. In the scheme polaron charge and spin are indicated by + and arrow, respectively. Gray shaded ellipses indicate trap sites accommodating P^+ or bipolarons. From left to right polarons form weakly coupled spin pairs in a mixed singlet (S) triplet (T) state upon encounter of mobile and trapped polarons. Resonant mw excitation alters the S and T content, with an oscillation frequency Ω (no spin locking) or 2 Ω (spin locking). ISC transfers population from T^0 to S. Depending on the S and T content of the pair, either triplet P^+P^+ pairs (transport blocked) or bipolarons (transport allowed) are formed.

increasing length. Depending on the underlying transport mechanism this may either increase or decrease the observed current, which shows a maximum (minimum) when the pulse spin flip angle reaches π, provided that the mw field only manipulates the spin state of one constituent of the spin pair. When the mw pulse length is increased further, the initial situation ($|\uparrow\uparrow\rangle$ or $|\downarrow\downarrow\rangle$) is partially restored and the signal decreases (increases) again. In consequence the pEDMR signal shows periodic oscillations reflecting the coherent spin motion during the pulse at the Rabi frequency Ω.

Upon increasing B_1 the Rabi frequency increases, and a second frequency component at 2 Ω is observed, Fig. 2(b). The intensity of this component increases monotonically with increasing B_1 until the amplitudes of both frequency components are equal at 1.0 mT. The power level at which the second frequency appears [$\sim$ 0.36 mT, cf. Fig. 2(a)] approximately coincides with the change of the pEDMR spectra shown in Fig. 1(b). These observations show unambiguously that spin locking of (initially) weakly coupled pairs of $S = 1/2$ particles is occurring, and that these are responsible for the spin-dependent transport process giving the EDMR spectrum.

In the absence of spin locking the mw field directly induces transitions between the singlet and triplet states (which are not necessarily eigenstates) at the Rabi frequency Ω. Spin locking decouples the singlet state from the triplet manifold so the shift in population is restricted to be within the three triplet states. These changes occur at 2 Ω (see Fig. 3) [20]. In the presence of intersystem crossing (ISC) between S and T^0 the singlet and triplet populations tend to equalize. ISC may be, e.g., caused by hyperfine interactions between polaron and nuclear spins. The link for population transfer between S and T^0 is thus partially reestablished. However, in this case the singlet content of the spin pair oscillates at 2 Ω, since the T^0 state content is varying at this frequency, and these changes manifest in the spin-dependent current changes.

By establishing that the EDMR spectrum is due to weakly coupled pairs of $S = 1/2$ particles we eliminate processes such as quenching of triplet excitons by polarons [7,22], or mutual annihilation of two triplet excitons [23], both of which could give a cwEDMR spectrum comparable to Fig. 1(a). The g value has eliminated possible involvement of fullerene polaron states. The agreement of the value with that for positive polarons, and the device characteristics which preclude significant P^- concentrations in MEH-PPV, lead to the conclusion that the spin-dependent transport process is positive bipolaron formation. We note that bipolaron formation may result in either current enhancement [8], as observed here, or quenching [8,13,24].

Two observations can be further analyzed, the two-component nature of the cwEDMR spectrum [Fig. 1(a)], and the detailed form and intensity distribution of the Rabi oscillations shown in Fig. 2. We infer from Fig. 1(a) that two different P^+ populations are detected, and are expected to be relevant to the transport mechanism. To verify that both populations contribute to the Rabi oscillations, we simulated the B_1 dependence of the coherent spin motion assuming the bipolaron model in which spin pairs are formed between one polaron from the narrow EDMR line, obtained from the fit shown in Fig. 1(a), and one from the broad EDMR line. We find that the simulation results agree well with the experimental data [Fig. 2(a)]. In contrast, there are clear deviations when the spin pairs are constrained to form only from within the broad or from the narrow EDMR line [14]. These results support the model in which the spin-dependent positive bipolaron formation

involves partners with dissimilar environments and/or mobilities and accordingly different line shapes in the cwEDMR spectrum. It should also be noted that the bipolaron model automatically concurs with the observation that the two components of the cwEDMR spectrum have equal intensities.

A mechanism which is consistent with this model is trap-mediated isoenergetic hopping. Deep level transient spectroscopy detects a hole trap 0.3–4 eV above the HOMO [25]. If the energy of the mobile P^+ and the doubly occupied bipolaron state is similar, isoenergetic hopping can occur. The final energy of the bipolaron state will be reduced by the correlation energy, which has been reported to be $\sim$0.2eV [26], and may thus be compatible with the trapping energy. The bipolaron formation process in accordance with our EDMR results is shown in Fig. 3: mobile P^+ drift in the electric field provided by the bias voltage. When a mobile P^+ encounters a trapped P^+, a P^+P^+ pair forms. Depending on the relative spin orientation of both carriers, the mobile P^+ may or may not hop to the site of the trapped P^+ to form a bipolaron. Since the hopping process occurs predominantly along the direction of the electric field, it results in a current enhancement and consequently yields a positive EDMR signal [8]. It is conceivable that the bipolaron is stabilized by a negative charge on an adjacent PCBM molecule [27].

Recently, McCamey *et al.* reported an EDMR study on MEH-PPV at $T = 10$ K [28]. As in Ref. [16] the authors interpreted their signal to arise from spin-dependent P^+P^- pair recombination. In our case, we can rule out this process for two reasons. (1) McCamey *et al.* injected charges at a bias voltage of approximately 15 V. This voltage is sufficient to inject electrons and holes into the polymer, as evidenced by the observation of electroluminescence. However, we used a bias voltage of 1 V which prevents the injection of electrons into the polymer. This bias is also close to the operating conditions of solar cells. (2) In Ref. [28] pure MEH-PPV was used. Thus, once an electron is injected into the polymer, it will either recombine or will be transported towards the electrodes. In contrast, in our work PCBM acts as a strong electron acceptor. As a result, negative polarons will be removed from the polymer phase, preventing recombination.

The observed process impacts solar cell operation; after optical generation of an exciton and subsequent separation into P^+ and P^-, the positive polaron is transported towards the ITO electrode. If another (trapped) P^+ with parallel spin orientation is encountered, the transport path involving positive bipolaron formation is blocked, so hindering charge transport to the electrode, and hence lowering the efficiency of the solar cell.

In conclusion, we have observed spin-coherent Rabi oscillations at room temperature persisting for times greater than 150 ns in a MEH-PPV:PCBM organic solar cell, using pEDMR. The observation of spin locking at high mw field values shows that weakly coupled $S = 1/2$ spin pairs are responsible for the spin-dependent current. The g value of the resonance indicates that the transport process is due to polarons in the MEH-PPV phase, and rules out the involvement of PCBM. The negligible population of negative polarons in MEH-PPV excludes recombination mechanisms. It is concluded that the EDMR spectrum is due to spin-dependent formation of positive bipolarons in MEH-PPV, where the spin-pair partners originate from different polaron populations. Finally, we note that the frequency independence of EDMR (to first order) [29] may allow measurements at field values used to observe MR in organic materials.

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